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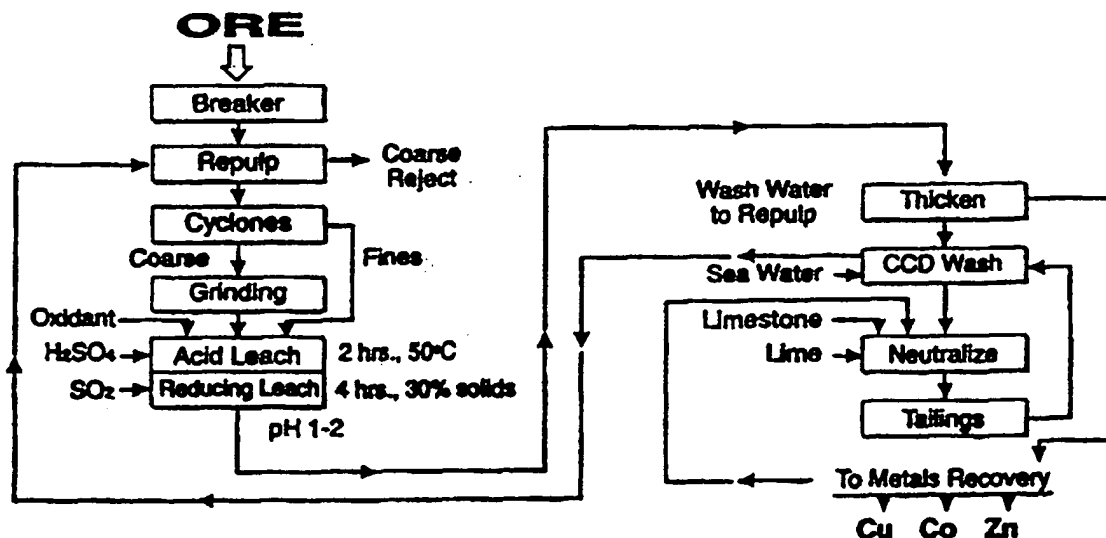
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(54) Title: HYDROMETALLURGICAL EXTRACTION OF COPPER, ZINC AND COBALT FROM ORES CONTAINING MANGANESE DIOXIDE



(57) Abstract

A method is provided for extracting copper, cobalt and zinc from an ore containing those metals and manganese dioxide. The ore is subjected to an acid, oxidizing leach followed by an acid, reducing leach. Solids are separated from the leachate and the leachate liquid is subjected to solvent extraction steps, to sequentially remove copper, zinc and cobalt in that order.

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HYDROMETALLURGICAL EXTRACTION OF COPPER, ZINC AND COBALT FROM ORES CONTAINING MANGANESE DIOXIDE

BACKGROUND OF THE INVENTION

This invention relates to a method of extracting copper, cobalt and zinc from an ore containing those
5 metals and manganese dioxide.

Copper, cobalt and zinc are known to occur in ores that also contain manganese dioxide. Such an ore occurs in the Boleo mine in Baja, Mexico. The present invention was developed treating an ore from that mine.

10 In a particular aspect the invention relates to the direct leaching in saline of an ore containing manganese dioxide and oxides and sulfides of copper, zinc and cobalt with subsequent recovery of metal values by solvent extraction and either electrowinning or
15 precipitation from the resulting leachate.

The Boleo mine has both oxide-and sulfide-dominant zones. The oxide ores contain copper as oxide and basic salt minerals and cobalt in manganese dioxide (pyrolusite). Iron oxide phases containing cobalt,
20 copper and some zinc are also believed to be present.

The sulfide ores contain copper as secondary copper sulfides (chalcocite and covellite) with minor primary mineralization (chalcopyrite). Cobalt and zinc are contained partly in sulfide phases. The sulfide ore
25 zones are lower in manganese dioxide.

The ore presents difficulties in the extraction of copper, cobalt and zinc and the present invention addresses those difficulties to provide excellent yields of those values.

30 Prior art known to applicant is as follows:

Thomas G. "The leaching of Manganese from Pyrolusite Ore by Pyrite", Canadian Journal of Chemical Engineering, February 1958, pp.37-43, describes the oxidation of a sulfide mineral (in this case pyrite) by manganese dioxide in a pyrolusite ore. Thomas does not describe a process that addresses the co-occurrence of cobalt and zinc.

U.S. Patent 5,232,490 issued August 3, 1993 describes the use of manganese dioxide to oxidize a precious metal ore, optionally in a chloride environment. The objective was to use manganese dioxide as an oxidant to decompose pyrite containing gold or silver. Manganese dioxide is also used to oxidize gold in the chloride environment. The chloride ion is used to complex the gold as a complex which can then be recovered by precipitation on activated carbon. Thus this patent teaches an oxidative leach using manganese dioxide in a chloride environment.

The abstract of Chinese Patent 87102046, dated December 9, 1987 teaches a reaction of manganese dioxide with pyrite to produce a manganese sulfate solution for the recovery of manganese. The use of manganese dioxide to oxidize a sulfide mineral is again illustrated.

The abstract of Soviet Patent 836166 dated June 7, 1981, describes the oxidative leaching of a copper sulfide ore using manganese dioxide and ferric chloride acidified with hydrochloric acid. Soviet Patent 626956 issued October 30, 1979 has a similar disclosure.

U.S. Patent 4,026,773 teaches the leaching of sea bed ores, in this case in the form of manganese nodules, using hydrochloric acid. Free chlorine gas is produced followed by a complicated solvent extraction/precipitation process to recover metals. The

process is deemed unattractive in the environment where the present invention is useful because of excess acid consumption, the high cost of hydrochloric acid and the release of free chlorine.

- 5 U.S. Patent 5,279,802 issued January 18, 1994 teaches the use of manganese dioxide to oxidize a sulfide ore.

U.S. Patent 4,740,243 issued April 26, 1988 teaches oxidation of sulfide minerals by manganese dioxide.

- 10 The abstract of Chinese Patent 85101961 issued September 3, 1986 teaches the recovery of molybdenum, bismuth and copper from a tungsten ore. The essence of that process appears to be the oxidation of bismuth sulfide with manganese dioxide and hydrochloric acid.

- 15 The abstract of Soviet Patent 836166 dated June 7, 1981 describes the leaching of sulfide ores containing non-ferrous metals (principally copper) with manganese dioxide as an oxidant.

- 20 The abstract of Indian Patent 140551 of November 27, 1976 describes the oxidation of zinc sulfide concentrates with manganese dioxide to leach the zinc.

The abstract of Polish Patent 92075 issued December 15, 1977 describes the leaching of copper concentrates with manganese dioxide and sulfuric acid.

- 25 The abstract of Japanese Patent 49021009 dated May 29, 1974 teaches the oxidation of bismuth sulfide with manganese dioxide and hydrochloric acid.

- 4 -

U.S. Patents 5,246,684 and 5,244,491 relate to zinc extraction from brines. The zinc forms anionic complexes in solution that can be extracted with anion exchangers.

Canadian Patent 1,021,574 issued November 29, 1977
5 describes the extraction of cobalt with an extractant, Aliquat 336, in the thiocyanate form. The patent teaches separation of cobalt from nickel in a sulfate solution.

O'Neill et al, "Purification of Nickel-Containing Process Streams by Aliquat 336 Thiocyanate", CIM
10 Bulletin, October, 1976, teaches the separation of nickel by the use of Aliquat 336 thiocyanate.

SUMMARY OF THE INVENTION

The present invention relates to a method of recovering copper, zinc and cobalt from a mixed oxide and
15 sulfide ore body containing sufficient manganese dioxide to oxidize the metal sulfides contained in the ore. The method provides for two sequential leaching steps followed by metal recovery process.

More specifically the present invention provides a
20 method of extracting copper, cobalt and zinc values from an ore containing said values and manganese dioxide that comprises:

subjecting the ore to an acid, oxidizing leach;
subjecting the ore to an acid, reducing leach;
25 subjecting the leachate to solid-liquid separation;
subjecting the liquid from the solid-liquid separation to solvent extraction for the metals copper, cobalt and zinc.

The metals may be thereafter recovered from their
30 respective extractants.

The sequence of the leaches is important. The oxidizing leach must precede reduction in order that the oxidizing

capacity of manganese dioxide in the ore is used. Also, solvent extraction will require that the leachate be reduced.

5 The leaching may be carried out in a saline medium as a source of water and chloride ion. Preferably, the saline medium is at least as saline as sea water and sea water or a sea water concentrate may be used.

10 The acid, oxidizing leach may be carried out with sulfuric acid and with manganese dioxide in the ore acting as the oxidizing agent. In some situations addition of manganese dioxide or increase in manganese dioxide content by blending of ore containing copper, cobalt and zinc with ore containing manganese dioxide may be desirable in order to provide sufficient oxidizing
15 agent.

The acid, reducing leach may be carried out with sulfuric acid and a suitable reductant, such as sulphur dioxide, sulphite or bisulphite.

20 The solid-liquid separation may be carried out by various means known in the art, including filtration and centrifugation. Solid-liquid separation may also be carried out in a thickener apparatus. Separated solids may be washed according to known processes such as counter-current decantation.

25 The metals are preferably recovered from the leachate liquid in the following sequence: copper, zinc then cobalt. The copper may be extracted by an organic solvent extraction using hydroxyoxime. The resulting organic solution containing copper may be washed to
30 remove entrained chloride, stripped by contact with an acid solution and treated by electrowinning to recover copper.

It may then be desirable to treat the liquid leachate to remove residual copper prior to zinc extraction. Treatment of residual copper may, for example, be carried out by adding a source of sulphide ion such as sodium sulphide, hydrogen sulphide, or sodium hydrogen sulphide to precipitate copper sulfide. Percipitated copper sulfide may be combined with fresh ore and re-leached.

The copper depleted liquid leachate may be treated with a quaternary ammonium compound in organic solvent to extract zinc. The quaternary ammonium compound may be a chloride or a thiocyanate. Those compounds available under the trademark Aliquat 336 have proved useful. The organic solution product of the treatment with the quaternary ammonium compound may be scrubbed with a zinc-containing solution to displace co-extracted impurities, which could include residual copper, as well as cobalt, manganese, and iron. The scrubbed organic solution may then be stripped with an ammonia solution to displace the zinc. An alkali compound such as sodium carbonate may be used to precipitate the zinc compound and to regenerate ammonia.

The cobalt may be extracted from the copper and zinc depleted leachate liquid with quaternary ammonium thiocyanate. The cobalt may be stripped from the resulting extractant by metal displacement. Metal displacement may be carried out by use of a high concentration zinc solution to displace cobalt, iron and manganese present. The cobalt strip-solution may be thereafter treated by further solvent extraction (eg. again by quaternary ammonium thiocyanate) with the resulting extract then being subjected to electrolysis to obtain cobalt. The electrolysis may be carried out in a diaphragm cell.

Washed solids from the above described solid-liquid separation processes, and the liquid leachate after the cobalt extraction may be combined and sent to neutralization and then to tailings.

5 BRIEF DESCRIPTION OF THE DRAWINGS

The invention is illustrated in figure 1 which is a flowsheet, and in the following detailed description of a preferred embodiment.

10 As shown in Figure 1, ground ore and fines are subjected to sequential oxidative and reductive leaching. The total leachate passes to a solid-liquid separation and counter-current decantation (CCD) circuit. Seawater may be used for the CCD wash. The solid leach residue is neutralized and is disposed of. The liquid leachate from
15 the aforementioned circuit is extracted with a hydroxyoxime extractant sold under the trademark LIX 984, to extract copper. The resulting organic extractant is scrubbed and stripped and the resulting copper solution subjected to electrowinning to produce LME grade copper.

20 The leachate liquid may then be treated to remove residual copper, using, in a preferred embodiment, sodium hydrogen sulfide. The copper sulfide precipitated is fed back to the oxidative and reductive leaching stages.

25 The copper depleted liquid leachate is extracted with Aliquat 336 in the chloride or the thiocyanate form in organic solvent, to extract zinc. Zinc is loaded to the Aliquat 336 solution and is subsequently stripped with ammonia. Sodium carbonate may be added to the resulting aqueous solution to precipitate zinc carbonate.

30 Finally, cobalt is extracted with an organic solvent containing Aliquat 336 in the thiocyanate form (Aliquat

336 SCN). The resulting cobalt depleted leachate may be fed to effluent. The cobalt containing extractant may be stripped again with Aliquat 336 SCN. The cobalt is thereafter extracted by adding a zinc sulfate solution.

- 5 The resulting cobalt solution may then be passed to cobalt recovery, which may be electrolysis in a diaphragm cell. Zinc may be recovered from the zinc loaded Aliquat 336 SCN organic solution by stripping with ammonia and subsequent precipitation of zinc carbonate through
- 10 addition of sodium carbonate. Ammonia may be distilled from the solution leaving a solution of sodium sulfate and sodium chloride as a by-product.

- The leaching of copper, along with some cobalt and zinc, from oxide ores is readily accomplished using
- 15 simple acid leaching at high acidity, for example at pH 1.1. To leach the bulk of the cobalt in most oxide samples, a reductive acid leach with sulphur dioxide at high acidity (about pH 1) is suitable. The reductive leach decomposes the manganese dioxide phases, releasing
- 20 metals that were trapped in the pyrolusite lattice. For some samples it has been found that a high temperature, high acid, atmospheric leach is capable of dissolving residual cobalt, copper and zinc contained in more refractory iron phases.

- 25 The leaching of sulfide ores is more difficult but sulfide minerals treated as shown in Figure 1 are reactive under reasonably oxidizing acid leach conditions. It is known in the art that chalcocite and covellite are leached in an acid system in the presence
- 30 of ferric ion. In an acid, oxidizing leach with manganese dioxide as the oxidant, the manganese dioxide will regenerate ferric ion in situ, thus leading to a rapid and complete leach of copper sulphide and other sulphide phases. Therefore the sulfide ore is first
- 35 subjected to an oxidizing leach to leach sulfide phases

followed by a reducing leach to decompose metal
containing manganese dioxide phases. Again if the more
refractory iron phases are present, a high temperature,
high acid, atmospheric leach can decompose these phases
5 and leach the contained metals.

The chemistry of the oxidizing leach and the
reducing leach is as follows:

Oxidizing Leach: $\text{MnO}_2 + \text{MS} + 4\text{H}^+ \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} + \text{M}^{2+} + \text{S}$
where M is Cu, Zn or Co.
10 Reducing Leach: $\text{MnO}_2 + \text{SO}_2(\text{g}) \rightarrow \text{Mn}^{2+} + \text{SO}_4^{2-}$
where metals contained in MnO_2 are
leached.

The leaching process may be carried out in seawater
as this is a readily available source of water and the
15 chloride ion in seawater is an aid to the oxidative
leaching. A typical temperature is in the range 50 - 70°C
and the pH is preferably in range 1 - 2. Manganese
dioxide contained in the ore has been found to be a
suitable oxidant for decomposing the sulfide phases.

20 The following examples illustrate the leaching step.

Example 1. Reducing Leaches on Oxide Samples.
Reducing leach conducted at 50°C in double strength
seawater for 4 hours at pH = 1 in the presence of an
excess of sulfur dioxide.

Chemical Analysis (%)						
Sample	Cu	Co	Zn	Fe	Mn	S(2-)
Head (Hole 28)	1.24	0.170	0.18	8.0	3.84	0
Residue	0.212	0.034	0.131	4.53	0.04	
Overall Metal Extraction	85.6	83.2	61.7	59.5	99.0	
Weighted Average of 10 Samples	89	83				

- 10 Example 2. Oxidizing and Reducing Leaches on Sulfide Samples. Oxidizing leach conducted at 50°C for 4 hours at pH ~ 1 in the presence of manganese dioxide. Reducing leach conducted at 50°C in double strength seawater for 4 hours at pH = 1 in the presence of an excess of sulfur
- 15 dioxide.

Chemical Analysis (%)						
Sample	Cu	Co	Zn	Fe	Mn	S(2-)
Head (Hole 115)	1.16	0.108	0.190	6.8	0.76	0.63
Reducing Leach Residue	0.36	0.072	0.121	5.4	0.04	
Oxidizing Leach Residue	0.108	0.024	0.090	6.2	**	
Overall Metal Extraction	92.1	81.1	59.7	22.5	**	
Weighted Average of 7 Samples						
Reducing Only	50	47				
Oxidative and Reducing	77	71				

** MnO₂ added to Oxidizing Leach

The values of cobalt and to some extent copper contained in the residue after oxidizing and/or reducing leaching are sometimes significant. It has been of interest in the metallurgical process development to attempt to bring this extra copper and cobalt into solution. The examples below summarize the sequential leaching of two oxide and sulfide samples respectively with an aggressive "iron leach" added to the sequence to ensure that all refractory iron phases and associated metals are adequately leached. All leaches conducted in the presence of double strength seawater.

Example 3. Sequential Leaches on Oxide Sample. Reducing leach conducted at 50°C in double strength seawater for 4 hours at pH = 1 in the presence of an excess of sulfur dioxide. Iron leach conducted at 100°C in double strength seawater containing 100 g/L H₂SO₄ for 4 hours.

Chemical Analysis (%)						
Sample	Cu	Co	Zn	Fe	Mn	S(2-)
Head (Hole 115)	4.44	0.092	0.450	12.1	1.76	0
Reducing Leach	0.516	0.040	0.386	8.18	0.05	
Residue						
Oxidizing Leach	Not	Req'd				
Iron Leach Residue	0.012	0.00	0.006	0.40	0.02	
Overall Metal Extraction	92.8	>95	98.1	99.5	99.2	

Example 4. Sequential Leaches on Sulfide Sample. Reducing leach conducted at 50°C for 4 hours at pH = 1 in the presence of an excess of sulfur dioxide. Oxidizing leach at 50°C and pH = 1 in the presence of an excess of manganese dioxide. Iron leach conducted at 100°C with leach solution containing 100 g/L H₂SO₄ for 4 hours in the presence of an excess of sulfur dioxide. All leaches conducted in double strength seawater.

Chemical Analysis (%)						
Sample	Cu	Co	Zn	Fe	Mn	S(2-)
Head (Hole 115)	1.60	0.132	0.25	6.33	3.24	0.57
Reducing Leach	1.60	0.134	0.199	4.72	0.16	
Residue						
Oxidizing Leach	0.448	0.048	0.060	4.17	**	
Iron Leach	0.022	0.034	0.002	0.71	0.00	
Residue						
Overall Metal						
Extraction	99.5	90.1	99.6	94.1	98.1	

** MnO₂ added to Oxidizing Leach

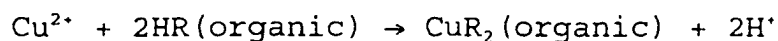
Clearly from inspection of the data in Examples 1 - 4, a combination of oxidative and reductive acid leaching will be necessary to maximize recovery of metals to solution for oxide and sulfide.

The leach solution from the solid-liquid separation and CCD wash circuit contains the species Cu²⁺, Co²⁺, Zn²⁺, Fe²⁺, Mn²⁺. Solvent extraction is used to selectively recover copper, zinc and cobalt from the clarified liquid leachate.

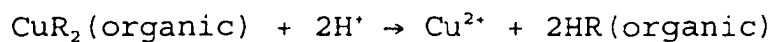
Copper Recovery

The solution entering solvent extraction for copper should be of the order of pH ~ 1.5. At this pH, LIX 984 (represented as HR below), extracts the copper (2+) ion very strongly from solution.

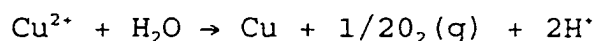
Solvent Extraction (Loading)



Solvent Extraction (Stripping)



Electrowinning



Copper Depletion

It may be desirable to further reduce the copper concentration in the feed prior to zinc solvent extraction as copper would be co-extracted with zinc by Aliquat 336. A cost effective way to do this is by copper sulfide precipitation.

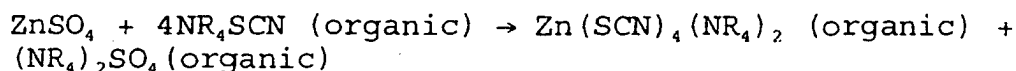


A suitable place for the impure copper sulfide product to be retreated is in the leach process. This would allow that copper to be subsequently recovered through the process of this invention.

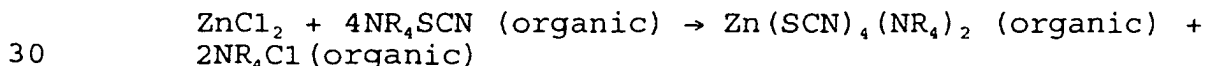
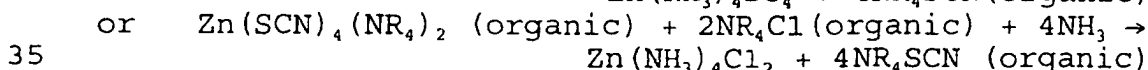
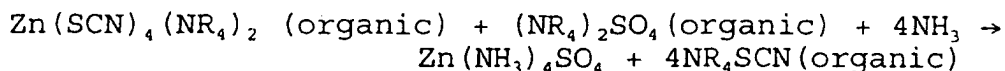
Zinc Recovery

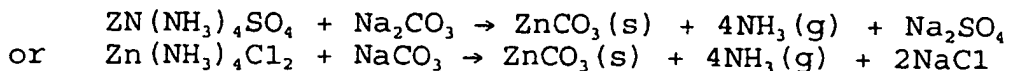
The recovery of zinc is through solvent extraction with Aliquat 336 either in the thiocyanate form (represented as NR_4SCN below) or in the chloride form (represented as NR_4Cl below). The zinc is loaded as a salt from the solution (eg. zinc sulfate or zinc chloride). The zinc is then stripped using ammoniacal solution to produce a zinc-ammonia complex. Finally zinc is precipitated with sodium carbonate to produce zinc carbonate and a solution of sodium sulfate-sodium chloride.

Using Aliquat 336 in the Thiocyanate Form Results in the Following Chemistry

25 Solvent Extraction (Loading)

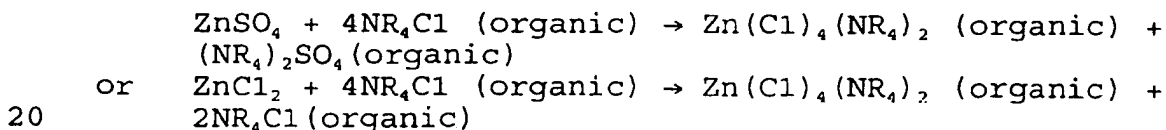
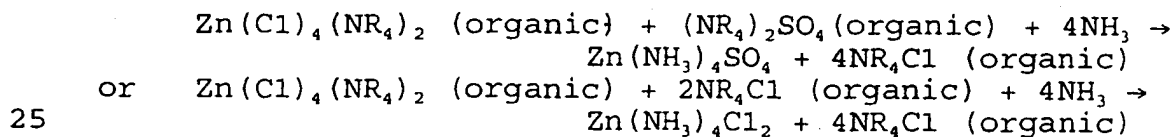
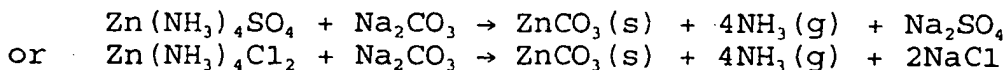
or

Solvent Extraction (Stripping)

Precipitation

The zinc carbonate precipitate may be of substantial
 5 purity. In laboratory testing of the zinc solvent
 extraction process, a 30% Aliquat 336 - SCN solution was
 loaded to 16.1 g/L Zn. The only contaminants noted using
 liquid leachate from Boleo ore in the laboratory have
 been Co (<0.5 mg/L) and Fe (0.9 mg/L). The zinc carbonate
 10 product may be acceptable to an electrolytic zinc plant
 as a feed to a leach circuit. This step also regenerates
 ammonia which may be recycled after distillation recovery
 from the zinc depleted liquid leachate.

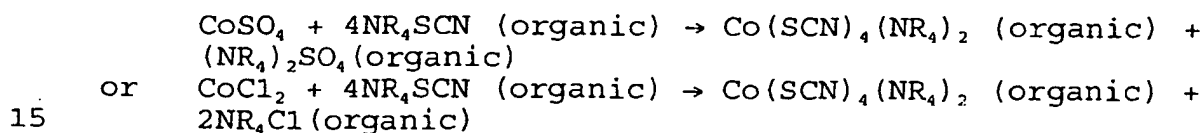
The following description illustrates the chemistry
 15 for zinc recovery using Aliquat 336Cl.

Solvent Extraction (Loading)Solvent Extraction (Stripping)PrecipitationCobalt Recovery

30 The extraction of cobalt is by the same chemistry as
 for zinc. The Aliquat 336 - SCN system is used for
 cobalt extraction. The recovery process may be
 complicated by the presence of iron, zinc or manganese on

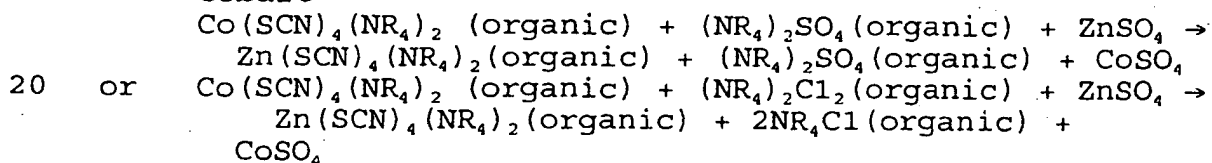
the loaded extractant. Cobalt, iron and manganese is stripped with a zinc sulfate solution. The resulting strip solution is treated for cobalt recovery by iron oxidation and hydrolysis, zinc solvent extraction or ion exchange and finally cobalt precipitation/redissolution/electrolysis. The stripped organic may still contain loaded zinc which must be removed before the organic can be reused for extraction of cobalt. The zinc removal process is referred to below as a regeneration step.

Solvent Extraction (Loading)

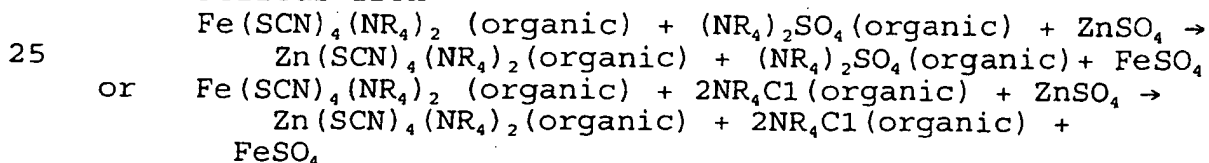


Solvent Extraction (Stripping)

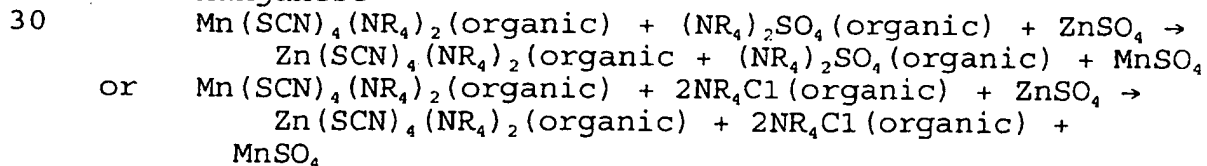
Cobalt



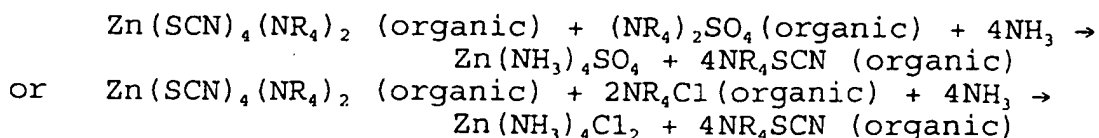
Ferrous Iron

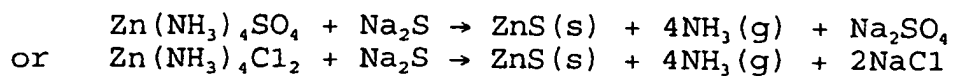


Manganese



Solvent Extraction (Regeneration)



Precipitation of Zinc

- While specific embodiments of the invention have
- 5 been described and illustrated, such embodiments should be considered illustrative of the invention only and not as limiting the invention as construed in accordance with the accompanying claims.

WE CLAIM:

1. A method of extracting copper, cobalt and zinc values from an ore containing said values and manganese dioxide that comprises:
 - 5 subjecting the ore to an acid, oxidizing leach;
 subjecting the ore to an acid, reducing leach;
 subjecting the leachate to solid-liquid separation;
 subjecting the liquid from the solid-liquid
10 separation to solvent extraction for the metals
 copper, cobalt and zinc.
2. A method as claimed in claim 1 in which the leach is carried out in a saline medium as a source of water and chloride ion.
3. A method as claimed in claim 1 in which the
15 acid, oxidizing leach is carried out with sulphuric acid
 with manganese dioxide in the ore acting as an oxidizing
 agent.
4. A method as claimed in claim 1 wherein
 manganese dioxide is provided by blending ore containing
20 said values with manganese dioxide containing ore.
5. A method as claimed in claim 1 in which the acid, reducing leach is carried out with sulphuric acid and a reductant selected from the group consisting of sulphur dioxide, sulphite and bisulphite.
- 25 6. A method as claimed in claim 1 in which the solid-liquid separation is carried out in a thickener apparatus.

7. A method as claimed in claim 1 in which the solid-liquid separation is followed by a counter-current decantation wash of solids.

8. A method as claimed in claim 1 in which the values are extracted in the sequence: copper; zinc; cobalt.

9. A method as claimed in claim 8 in which copper is extracted by organic solvent extraction using a hydroxyoxime.

10. A method as claimed in claim 9 that further includes washing a resulting copper loaded organic solution to remove entrained chloride, stripping with an acid solution, and electrowinning to recover copper.

11. A method as claimed in claim 9 including treating the liquid to remove residual copper after extraction with a hydroxyoxime and before extraction of zinc.

12. A method as claimed in claim 11 in which the residual copper is removed by adding a source of sulphide ion to precipitate copper sulphide.

13. A method as claimed in claim 12 in which the source of sulphide ion is selected from the group consisting of: sodium hydrogen sulphide, sodium sulphide and hydrogen sulphide.

14. A method as claimed in claim 12 in which copper sulphide precipitate is returned to fresh ore to be leached.

15. A method as claimed in claim 9 in which the liquid from which copper has been extracted is treated

with an organic solvent containing a quaternary ammonium compound to extract zinc.

16. A method as claimed in claim 15 in which the quaternary ammonium compound is a chloride or a
5 thiocyanate.

17. A method as claimed in claim 16 that further includes scrubbing a resulting zinc loaded organic solution with a zinc-containing solution and stripping with an ammonia solution to displace the zinc.

10 18. A method as claimed in claim 17 in which an alkali compound is used to precipitate zinc compound and to regenerate ammonia.

19. A method as claimed in claim 15 in which the liquid from which copper and zinc have been extracted is
15 treated with an organic solvent containing a quaternary ammonium thiocyanate, to extract cobalt.

20. A method as claimed in claim 19 that further includes stripping a resulting cobalt loaded organic solution by metal displacement.

20 21. A method as claimed in claim 20 in which metal displacement is carried out by contacting with a high concentration zinc solution to displace cobalt, iron and manganese.

22. A method as claimed in claim 21 in which
25 cobalt is extracted from a resulting cobalt containing solution by further solvent extraction and a resulting extractant is subjected to electrolysis to obtain cobalt.

23. A method as claimed in claim 22 in which the electrolysis is carried out in a diaphragm cell.

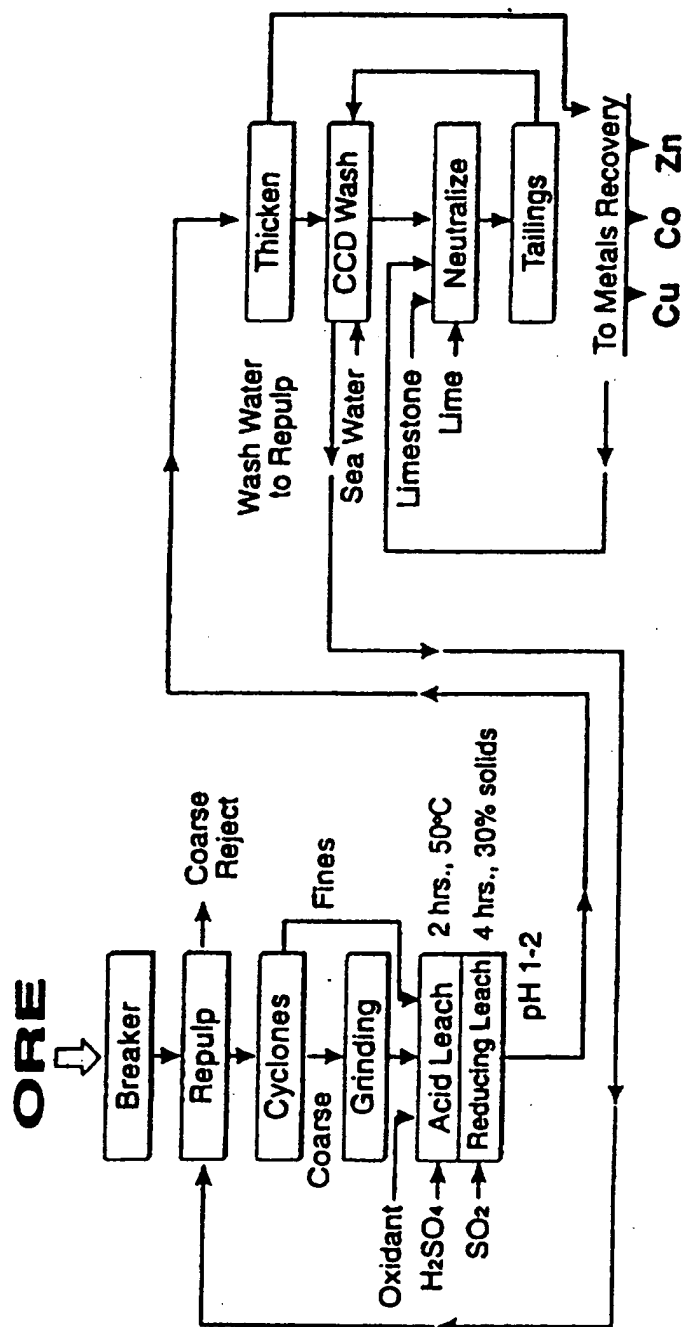


FIGURE 1